Synthesis, Characterization, and Catalytic Activity of Monometallic Pd and AgPd Bimetallic Nanoparticles in Different Solvent Media

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This is to certify that the dissertation entitled ***"Synthesis, Characterization, and Catalytic Activity of Monometallic Pd and AgPd Bimetallic Nanoparticles in Different Solvent Media"*** *being submitted by* ***Nilendri Rout*** *to the Department of Chemistry, National Institute of Technology, Rourkela, Odisha, for the award of the degree of Master of Science in Chemistry is a record of bonafide research work carried out by them under my supervision and guidance. I am satisfied that the dissertation report has reached the standard fulfilling the requirements of the regulations relating to the nature of the degree*.

Rourkela-769 008

Date:

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Supervisor

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Nilendri Rout

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CHAPTER 1

INTRODUCTION

1.1 General Introduction on Nanoparticles

Nanoparticles are particles which range from size of 1 nm to 10 nm having specific physical and chemical properties that are intermediate between those of the atomic element from which they are composed relative to those of the bulk metals [1]. One of the important properties of nanoparticle is that they can allocate high ration of atoms on their surface. Being very small in size they will have more defects i.e. more edges and kinks compared to larger particles. Stabilization of high –index crystal planes and alternative packing arrangement of atoms can also occur in small nanoparticles [2]. Nanoparticles may consist of identical atoms, molecules and two or more different species. Nanoparticles have distinct properties from those of individual atoms and molecules or bulk matter [3]. Nanoparticle are of great interest due to their size dependency of their properties, for example, silver in its bulk state is inactive but in *1970s Bond et al* worked on silver nanoparticle and they found it as effective catalyst in olefin hydrogenations [4] .

1.2 **Nanoparticle Catalysis**

Catalysis is a major field of nanoscience and nanotechnology [5]. Catalyst provides an alternative pathway in which the activation barrier of a reaction is lowered and the reaction rate is increased [6].

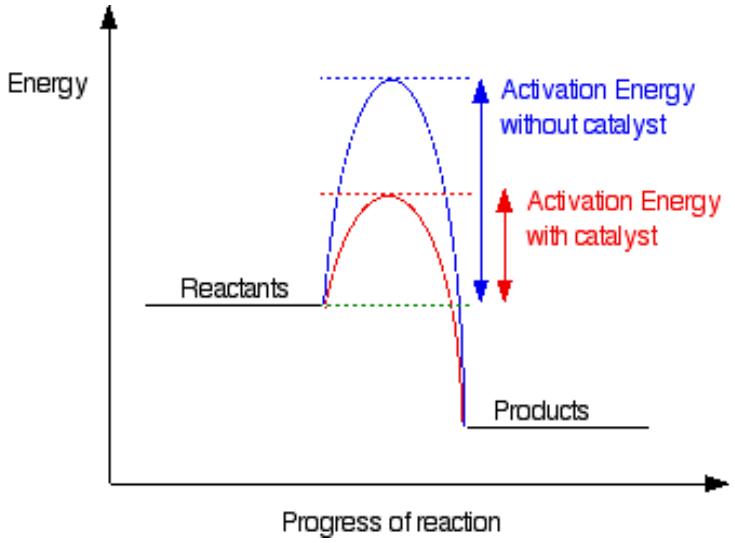


Fig.1. Reaction pathway with and without catalyst [6].

Catalysts are classified into three main categories: heterogeneous, homogenous and enzymatic but another type of catalyst has been known as quasi-homogeneous catalyst. Surface of nanoparticles are unstable and get precipitate out of the solution. So substances such as polymers, dendrimers, block copolymer, surfactant, and organic ligands are used to stabilize the metal nanoparticles. Catalysis by nanoparticles in solution is known as quasi-homogeneous catalysis and the catalyst as quasi homogenous catalyst [7]. Nanoparticles are being used as catalyst from 19^{th} century which was reported with nanoparticle with photography and decomposition of hydrogen peroxide using Platinum nanoparticles [8]. Pioneering catalytic application of nanoparticle was carried out in 1940 by Novrd et.al on the reduction of nitrobenzene and in 1970 by parravavano on hydrogen – atom transfer between benzene and cyclohexene and oxygen atom transfer between CO and CO_2 using Au nanoparticle. After these discoveries in 19^{th} century, nanoparticle attracts the researchers and large research activity has been going on to design nanocatalyst improving nanoparticle catalyst stability, activity, selectivity and mechanism. In 1970s, a new concept introduced the use of bimetallic in the preparation of nanoparticles which was developed by Toshimas's group who used PVP to stabilize core-shell bimetallic gold-palladium nanoparticles and gold in the core and the shell is palladium [8].

1.3 Synthesis of Monometallic and Bimetallic Nanoparticles

Bimetallic nanoparticle are of great interest than that of monometallic in both scientific and technological view as in bimetallic nanoparticle catalytic properties can be improve than that of the single metal catalyst [9].

Both bimetallic and monometallic nanoparticle can be prepared by different methods. Metal nanoparticle can be prepared by two ways by subdivision of bulk metals (a physical method) and growth of particle from molecular or ionic precursors (chemical method) [5]. The chemical method is more suitable than that of the physical methods as the size and uniformity of the metal nanoparticles can be controlled by the chemical method. Nanoparticle synthesized by physical method have broad particle size distribution (typically particle size greater than 10nm with distribution greater than 20 percent)[8]. Basically there are two approaches for nanoparticle synthesis top-down and bottom-up. The top-down method creates nanoscale objects by using larger and externally- controlled microscopic devices to direct their assembly. Bottom up approaches adopt molecular components that are built up into more complex assemblies [10].

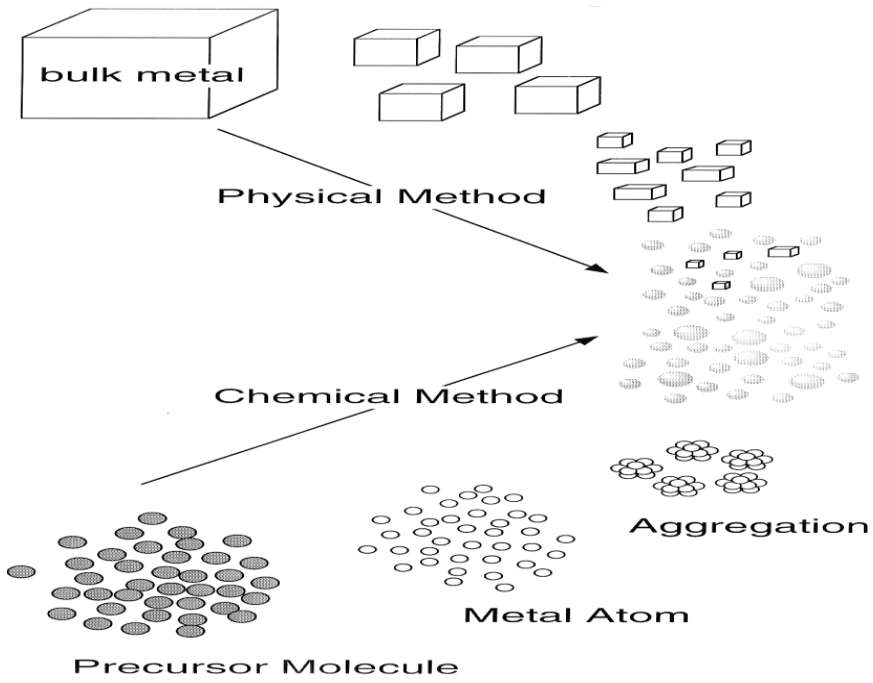


Fig. 2. Schematic illustration of preparative methods of metal nanoparticles [8]

Three major routes normally used in chemical synthesis of transition metal nanoparticles:

1) Chemical reduction
2) Thermal and photochemical decomposition
3) Electrochemical reduction [11].

1.3.1 Thermal and Photochemical Decomposition:-

Thermal decomposition involves pyrolysis of precursors in high boiling solvents at high temperature of ten in excess of 250-300 ˚C but the main disadvantage of this process is that under such condition, isolating highly reactive and unstable nanocrystal phases can be challenging. Photochemical method facilitates the generation isolation and study of metastable nanomaterial having unusual size, composition and morphology. Light induced reaction proceeds through alternative pathways at low temperature [12].

1.3.2 Electrochemical Reduction

Electricity is used as the driving or controlling force. Electrochemical synthesis is achieved by passing an electric current between two electrodes separated by electrolyte. The main advantages of electrochemical techniques includes avoidance of vacuum system as used in physical techniques, low cost, simple operations, high flexibility, and easy availability of equipment. This method widely used in many industrial applications [13].

1.3.3 Chemical Reduction:-

In this method, metal ions are reduced to zero valent state and co-ordination of stabilizing polymer to metal nanoparticles. In practice, reduction can be precedes or followed by the interaction between metallic species and polymers. If the reduction precede the interaction, the structural properties of thermal nanoparticles are determined only by the reduction condition but if the interaction precede the reduction, the interactive force between polymers and metal ions may affect the size and structure of metal nanoparticle [8].

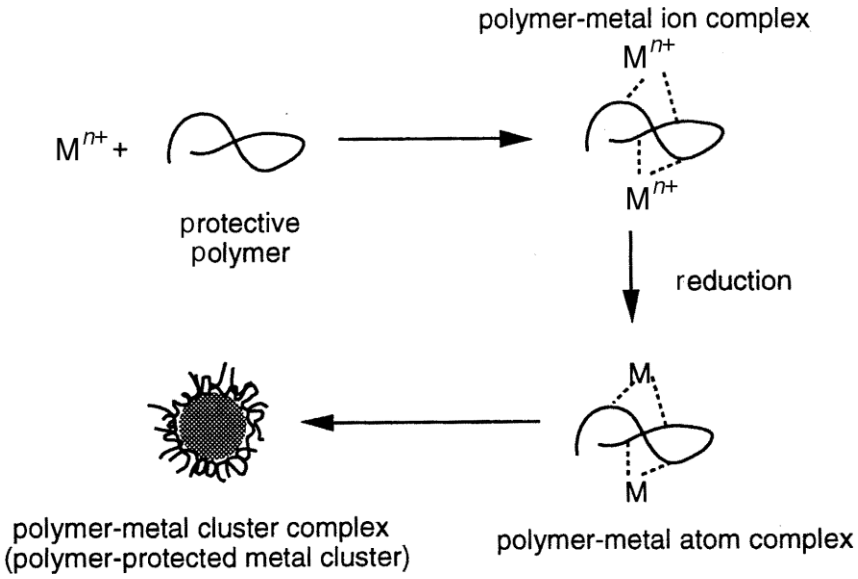


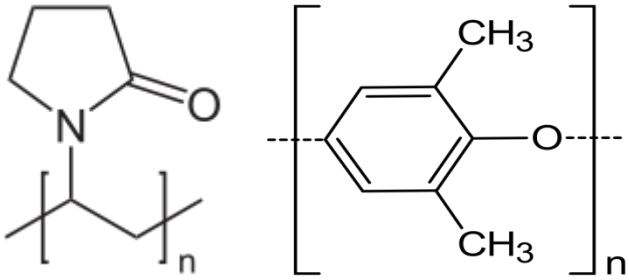
Fig.3. Schematic illustration of the reduction process of metal salts in the presence of a stabilizing polymer [8].

$NaBH_4$ or KBH_4 reduction methods have been widely used for the synthesis of Au, Ag, Pt, Pd and Cu nanoparticles [14,15]. The chemical reduction have following advantages; i) the method is very simple and reproducible, ii) particle size of the obtained metal nanoparticles is small with a narrow size distribution, iii) size of particle can be controlled by altering the preparative condition such as varying the concentration of metals, etc., iv) the obtained colloidal dispersion of metal nanoparticle show a high catalytic activity, and v) the obtained colloidal dispersion are stable and no precipitates normally observed for years [8].

1.4 Stabilizer for synthesis of nanoparticl synthesis

Nanoparticle surfaces are quite unstable and precipitate out of solution and lose their catalytic activity. The metal nanoparticles can be stabilized by using stabilizers like polymers, block copolymer, dendrimers, surfactants or organic ligands [18]. A polymer provides stabilization for metal nanoparticle sterically by the bulk of their framework and also by binding weakly to the nanoparticle surface through heteroatom that play the role of ligands. PVP (polyvinylpyrolidone) and PPO (poly (2, 5-dimethylphenylene oxide) mainly used for nanoparticle stabilization and catalysis as these two fulfill both steric and ligand requirement. Many other polymers have

recently been used as effective support for nanoparticle catalysis such as polyurea, polyacrylonitry / polyacrylic acid multilayer polymer [16].



PVP PPO

Fig.4. Structure of some common used polymer stabilizer

1.5 Types of Bimetallic Nanoparticles

Bimetallic nanoparticles are mainly of different types: cluster-in-cluster, core-shell and random alloy nanoparticle. In random alloy structure, the two different metals (A and B) are located completely at random. The structure of the alloy is controlled by parameters such as reduction kinetics of each metal, mole ratios and presence of external ligands. They all can play important roles in terms of whether or not alloy structures are realized. In core-shell structure, one metal forms the core and the other metal surrounds the core to form a shell. Core-shell structure formed by co-reduction and successive reduction methods. Core-shell is one of the important bimetallic structure as they have been used systematic investigations of electronic properties of catalysts and can potentially be used to minimize the amount of precious metals [17].

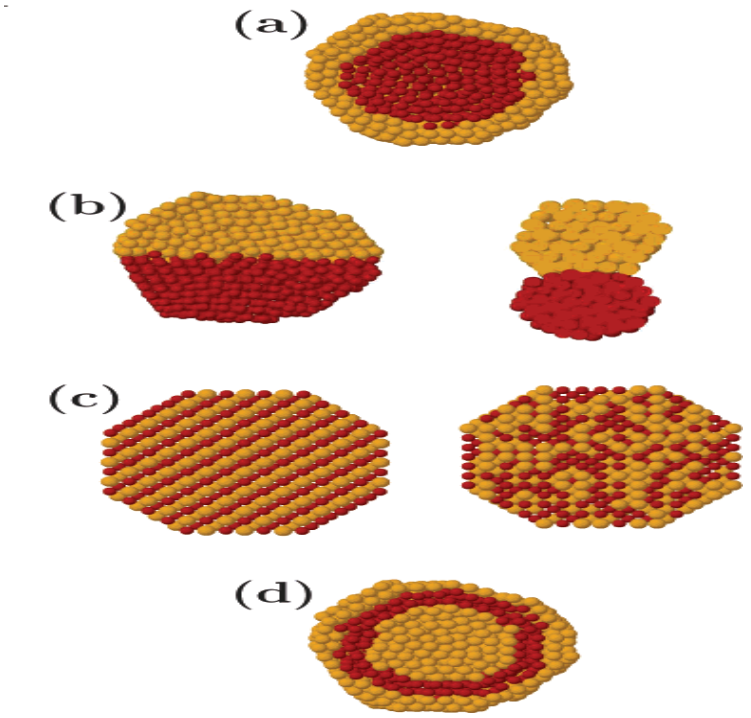


Fig.5. Schematic representations of some possible mixing patterns of bimetallic nanoparticles: core-shell (a), subcluster segregated (b), mixed (c), three shell (d). The pictures show cross sections of the clusters [17].

Sub cluster segmented alloy consists of A and B sub clusters, which may share mixed interface or may only have a small number of A-B bonds. This mixing patter is theoretically possible but no example has been known of this type. Multishell nanoalloy may be present like layered or onion-like alternating –A-B-A- shells. Metastable structures of this type were observed in simulations of the growth of Cu-Ag, Ni-Ag and Pd-Ag clusters. There are examples of stable A-B-A and A-B-A-B arrangements of Co-Rh and Pd-Pt clusters, respectively [17].

Bimetallic nanoparticles from metal salts can be prepared by two methods: co-reduction and successive reduction of two metal salts. Co-reduction is the simplest method for the preparation of bimetallic nanoparticle. The synthesis is same as the monometallic nanoparticle but the only difference is the number of metal precursors used in the co-reduction method [8].

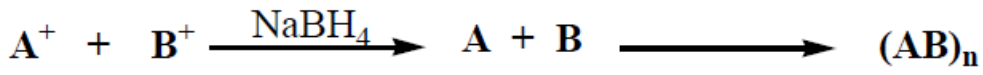


Fig.6. Schematic view of the synthesis of metal nanoparticles by co-reduction.

Successive reduction method is used to prepare "core-shell" structural bimetallic nanoparticle. In this method, one metal element is deposited on previously formed monometallic nanoparticle. So, the second element must be deposited on the surface of pre-formed particle [9].

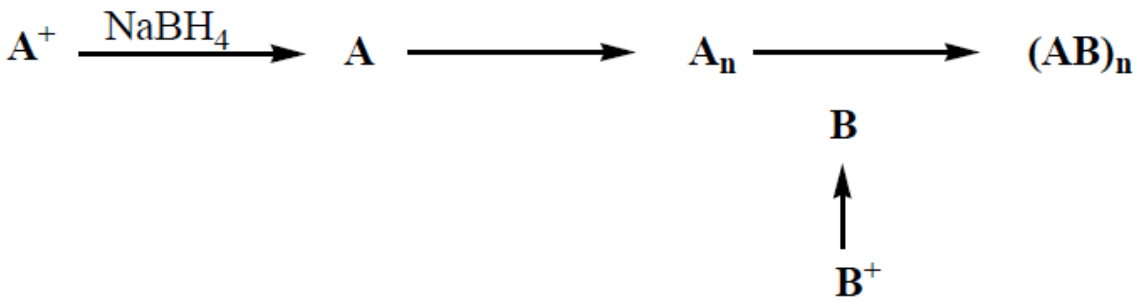


Fig.7. Schematic view of the synthesis of metal nanoparticles by successive reduction.

1.6 Characterization of Nanoparticles

Once metal nanoparticle has been synthesized, it is important to characterize their structure. Some of the commonly used characterization methods for nanoparticle catalyst have been shown below.

Table 1. Commonly used characterization methods for nanoparticle catalyst

Method	**Metal structure**
Light Scatteing	Size (core + ligand shell)
Small angle X-ray Scattering (SAXS)	Size (core + ligand shell)
Transmission Electron Microscopy (TEM)	Size (core), Morphology , Atomic coordinates
Energy Dispersive X-ray(EDS) Spectroscopy	Oxidation State, Electronic Interaction

X-ray diffraction (XRD)	Average coordination environments,bond distance
X-ray photoelectron Spectroscopy (XPS)	Oxidation state, Electronic Interaction
Extended X-ray Absorption Fine structure (EXAFS) Spectroscopy	Average coordination environment,bond distance
X-ray Absorption Near-Edge Structure (XANES) Spectroscopy	Oxidation state and orbital occupancy
Ultraviolet(UV)-Visible spectroscopy	Plasmon bands, presence of aggregates
Infrared (IR) Spectroscopy	Surface structure

1.7 AgPd as Catalyst

Palladium based alloys are always under investigation due to better solubility and permeability of hydrogen than the pure Pd. Specially AgPd alloy is under research investigation due to the high permeability for hydrogen [21] . AgPd nanoparticle also enhances selectivity, owing to the presence of the sub-surface Ag. AgPd alloy have excellent selectivity for the partial hydrogenation of acetylene to ethylene [22]. In the catalyst, Pd-rich surface function to dissociate H_2 and catalyze Hydrogenation reaction and Ag-rich core to present the occurrence of sub-surface hydrogen [23].

1.8 Ionic liquid as a Solvent

Ionic liquid can be defined as the family of the molten salts having melting point below 100 $^{\circ}$C. They can be typically organic salts or eutectic mixtures of an organic salt and an inorganic salt [24].

1.8.1 Ionic liquid as an Alternative Solvent to Water and Organic solvent

Water as a solvent has many drawbacks such as liquid range of water (0-100 $^{\circ}$C). Many organic solvents have low solubility in water. So water can't be used as a solvent for low and high temperature organic reactions. Organic solvents have low boiling point and high vapor pressure,

the solubility of inorganic reactants in these solvent is low, organic solvents are highly toxic, flammable and even explosive[24].

The general properties of ionic liquid that make them suitable to chemical synthesis and catalysis include [24]:

- They have no (or negligible) vapor pressure and therefore do not evaporate.
- They have favorable thermal properties.
- They dissolve many metal complex, catalysts, organic compounds and gases.
- They are immiscible with many organic solvent and water [25].

Transition metal nanoparticles in imidazolium-based ILs have been found to be active catalysts for various catalytic reactions. Some of the most common reactions where these metal nanoparticles have found applications are hydrogenations of aromatic rings, double bonds, and carbonyl groups and C-C coupling reactions such as Heck,Suzuki and Sonogashira reactions [26].

Previously many studies have been done about the synthesis and catalytic activity of AgPd nanoparticles in different medium such as water and ethylene glycol. However, to the best of our knowledge the use of AgPd nanoparticle in ionic liquid solvent has not been studied. In this project, our aim was to find a way to synthesize AgPd bimetallic nanoparticles in ionic liquids and use them in simple hydrogenation reaction. Also, our aim was to provide a comparative studies of AgPd nanoparticle in different solvent media. In this project work, $BMIMPF_6$ ionic liquid was used as solvent for the preparation of nanoparticle. AgPd bimetallic nanoparticles were prepared in different media such as water, ethylene glycol, and ionic liquid. The catalytic activity was measured for hydrogenation of allyl alcohol. The reusuability of the bimetallic catalyst after the reaction in ionic liquid was carried out.

1.9 Objectives of Present Work

The main objectives are

- Synthesis of Pd and AgPd nanoparticle in water, ethylene glycol and ionic liquid media.
- Characterization of the above synthesized nanoparticles by UV-Vis spectroscopy.
- Measurement of catalytic activity of these nanoparticle catalysts for allyl alcohol hydrogenation reaction.

Chapter 2

Materials and Methods

2.1 Materials

1-Methylimidazole (99%) and 1-chlorobutane (99.5%) were purchased from sigma aldrich and were distilled over KOH and P_2O_5 respectively, before use. Hexafluorophosphoric acid (*ca.* 65% solution.in water), poly(vinylpyrrolidone) (M.W. 40,000), Silver nitrate (A.R.grade, 99%) , potassium tetrachloropalladate (99.99%) and sodium borohydride powder (98%) were purchased from sigma Aldrich. Allyl alcohol (99%) were obtained from Hi-media and were used as obtained . Millipore water (18 mΩ) was used throughout the experiment.

2.2 Synthesis of Nanoparticle Catalysts

2.2.1 Synthesis of Palladium Nanoparticle in Water

Aqueous solution of PVP (0.0055) was taken in a round bottom flask. To it, aqueous solution of palladium salt (K_2PdCl_4, 0.0055mmol) was added. Then the whole solution was reduced using 0.052mmol of $NaBH_4$ as reducing agent and stirred for 20 min (at 400rpm).

2.2.2 Synthesis of Silver-Palladium(AgPd) Core Shell Nanoparticle in Water

The reaction stoichiometry(Ag/Pd salt ratio) was calculated using the method described in a previous work [22]. In the synthesis of core shell nanoparticle, the Ag to Pd salt ratio was taken as 2:1. First of all, PVP (0.0055mmol) was taken in a round bottom flask. 2 ml of distilled water was added to PVP and stirred for 15 min. To the solution of PVP aqueous solution of silver salt $AgNO_3$ (0.011mmol) was added. Then, the whole solution was reduced using aqueous solution of $NaBH_4$ (0.163mmol). Appearance of Golden yellow color showed the formation of Ag seed. After that the system was transferred to an oil bath maintained at 85 ºC temperature and then aqueous solution of palladium salt K_2PdCl_4 (0.0055mmol) was added dropwise for 15 min and stirred for 30 min (at 400 rpm). The total catalyst solution was made upto 5ml volume. The reaction was carried out in dark environment as silver is light sensitive.

2.2.3 Synthesis of Silver –Palladium (AgPd) Nanoparticle Using Ethylene Glycol

The reaction stoichiometry(Ag/Pd salt ratio) was calculated using the method described in previous work[22]. In the synthesis of core shell nanoparticle the Ag to Pd salt ratio is taken as 2:1.First of all, PVP(0.011mmol) was taken in a round bottom flask . 2ml of distilled water was added and stirred for 15 min. To the solution of PVP solution of silver salt in ethylene glycol $AgNO_3$(0.011mmol) was added then the whole solution was reduced using ethylene glycol. Appearance of golden yellow color showed the formation of Ag seed. After that aqueous solution palladium salt K_2PdCl_4 (0.0055mmol) solution in ethylene glycol was added dropwise for 15min and stirred for 30 min (400 rpm). The total catalyst solution was made upto 5ml volume. The reaction was carried out in dark environment as silver is light sensitive.

Palladium nanoparticle was synthesized in the same way as synthesized in water.

2.2.4 Synthesis of 1-Butyl-3-Methylimidazolium Hexaphosphate ($BMIMPF_6$) Ionic Liquid

BMIMCl (0.17mol) along with 40ml Millipore water was taken in round bottom flask. An aqueous solution of 65% HPF_6 in a 1:14 molar ratio was slowly added to the solution in an ice bath, to minimize the amount of heat generate. After HPF_6 was added, two layers were formed. The upper layer was decanted and the remaining product was washed with water several times,washings were tested with $AgNO_3$ until no AgCl precipitate was seen. Then the product obtained was dried at 70 ^{0}C under vacuum line for 4h to get the dried product. The purity of $BMIMPF_6$ was confirmed by ^{1}H NMR and UV-Vis spectroscopy.

2.2.5 Synthesis of Pd Nanoparticle in 1-Butyl-3-Methylimidazolium Hexaphosphate ($BMIMPF_6$) Ionic Liquid

Pd nanoparticles was synthesized in $BMIMPF_6$ in the following way. Initially, PVP (0.011mmol) was taken in 2ml of methanol, followed by addition of 2ml of a 0.0055mmol methanol solution of K_2PdCl_4. The mixture was stirred for 15min, followed by addition of 1.0ml of a 0.052mmol $NaBH_4$ solution in methanol. The methanol solution containing the nanoparticles was then added to 5ml of $BMIMPF_6$ IL, followed by removal of the methanol under vacuum. After 4h drying in vacuum, Pd nanoparticles in $BMIMPF_6$ ionic liquid was used for characterization and catalysis.

2.2.7 Synthesis of AgPd Nanoparticle in $BMIMPF_6$Ionic Liquid

0.011mmol of PVP was taken in 1ml ml of methanol, followed by the addition of 1ml of a 0.011mmol methanol solution of $AgNO_3$. The mixture was stirred for 15 min, followed by the addition of 1.0ml of a 0.163mmol $NaBH_4$ solution in methanol, which was prepared immediately before use. The formation of a golden yellow solution indicated the formation of Ag seed. Then, 2ml of a 0.0055mmol methanol solution of K_2PdCl_4 was added to Ag seed. The change of color from golden yellow to black indicates the formation of Ag-Pd nanoparticle. The methanol solution containing the nanoparticles was then added to 5ml of $BMIMPF_6$ IL, followed by removal of the methanol under vacuum. After 4h drying in vacuum, AgPd nanoparticles in $BMIMPF_6$ ionic liquid was used for characterization and catalysis.

The materials prepared in section 2.2.1, 2.2.2, 2.2.5, 2.2.6 were characterized by UV-Vis spectroscopy.

2.3 Catalytic Activity of Nanoparticles

Hydrogenation reactions were carried out in three-necked round –bottom flask at 40 ^{0}C. One end of the flask was connected to the H_2 gas source, the other end with the differential pressure gauge (model 407910, Extech instruments corp) and the central portion was closed with rubber septum. First 5ml of the catalyst solution was placed in the flask, followed by purging the system with H_2 for 10 min, after purging the H_2 source was closed and the system was stirred for 10 min to ensure equilibrium between the gas and solution phase and it was confirmed that there were no leaks in the system (H_2 was not consumed in the absence of substrate). Then substrate was taken (in ratio substrate:catalyst ratio=500:1). So when palladium nanoparticle was taken as catalyst 0.25ml of allyl alcohol was taken but when Ag-Pd nanoparticle was taken as catalyst 0.5ml of allyl alcohol was taken by syringe under vigorous stirring condition(at 1200 rpm), followed by measurement of the H_2 uptake via differential pressure measurement in every 10s. This in turn allowed calculating the turnover number (TON, mol of H_2/mol metal) of the catalyst system. The (TOF(mol H_2/mol metal) h^{-1}) was then determined from slope of linear plots of TON vs. time.[22]

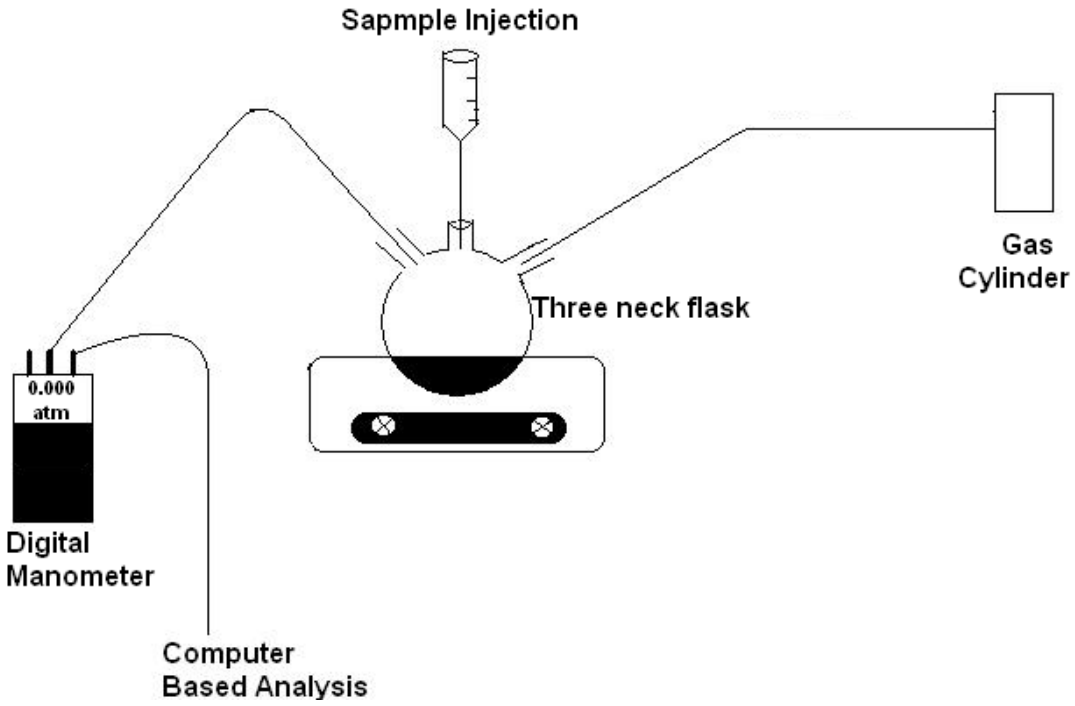


Fig. 8. Set up for the hydrogenation of allyl alcohol using the pressure mamometer.

Chapter 3

Results and Discussion

3.1 Characterization of Monometallic Pd and Bimetallic AgPd Nanoparticles

The UV-Vis spectra of Ag and AgPd core shell nanoparticle in water solvent are shown in fig.9 and the UV-Vis spectrum of Pd nanoparticle ins shown in fig 10 where we observed no peak for palladium. The UV-Vis spectra of silver and silver palladium peak shown above show a peak at 403 nm for silver nanoparticle due to surface plasmon resonance. However the UV-Vis spectrum of AgPd bimetallic nanoparticle is similar to that of Pd nanoparticle, and the surface plasmon resonance does not show any absorption peak. This may be due to that AgPd nanoparticle were totally encapsulated by surrounding Pd atoms and the Pd atom layer in the bimetallic nanostructure is thick enough to hide the characteristic plasmon peak of Ag.

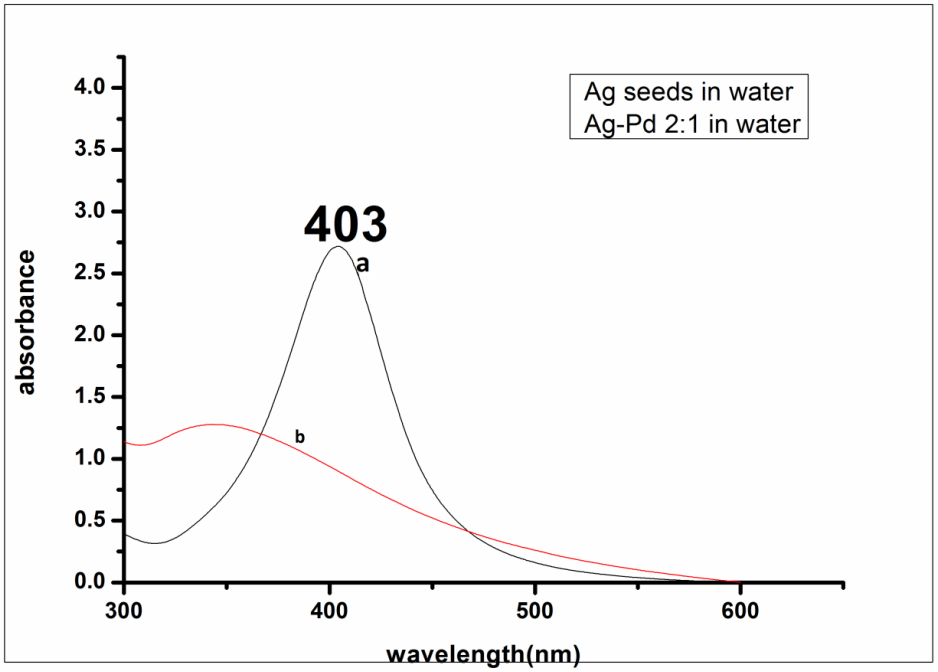


Fig.9. UV-Vis spectra of (a) Ag Nanoparticle in water,(b)Ag:Pd 2:1 Nanoparticle in water.

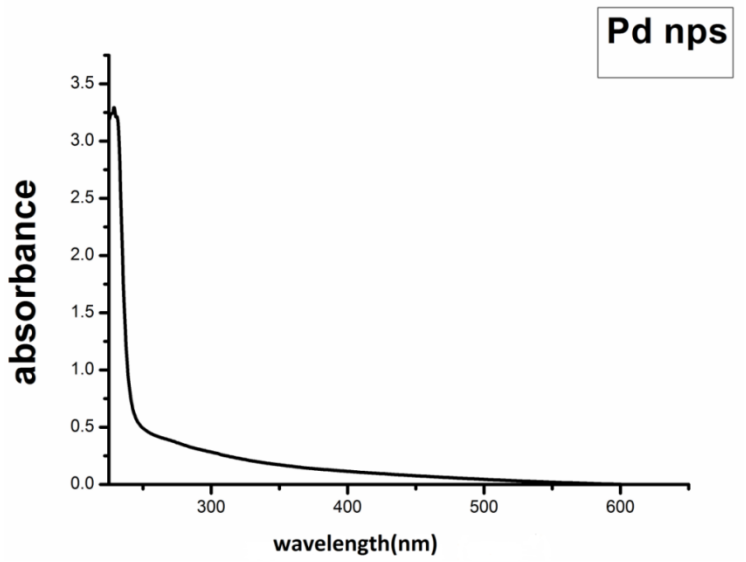


Fig.10. UV –Vis spectra of Pd nanoparticle(nps) in water

The above given UV-Vis spectra of Pd nanoparticle shows no peak because Pd nanoparticle does not resemble any surface plasmon resonance.

The purity of the synthesized $BMIMPF_6$ IL was checked by UV-Vis and ^1H NMR spectroscopy. The peaks clearly shows that $BMIMPF_6$ was obtained without impurities. The spectra shows all the proton NMR spectrum contained peaks corresponding to the imidazolium cation and indicated no residual reactants. ^1H-NMR($CDCl_3$, 400MHz): δ(ppm) = 8.29 (s, 1H, NCHN), 7.258 (d, 1H, $CH_3NCHCHN$), 7.22 (d, 1H, $CH_3NCHCHN$), 4.05 (m, 2H, $NCH_2(CH_2)_2CH_3$), 3.78 (s, 3H, NCH_3), 1.71 (m, 2H, $NCH_2CH_2CH_2CH_3$), 1.25 (m, 2H, $N(CH_2)_2CH_2CH_3$), 0.816 (t, 3H, $N(CH_2)_3CH_3$).

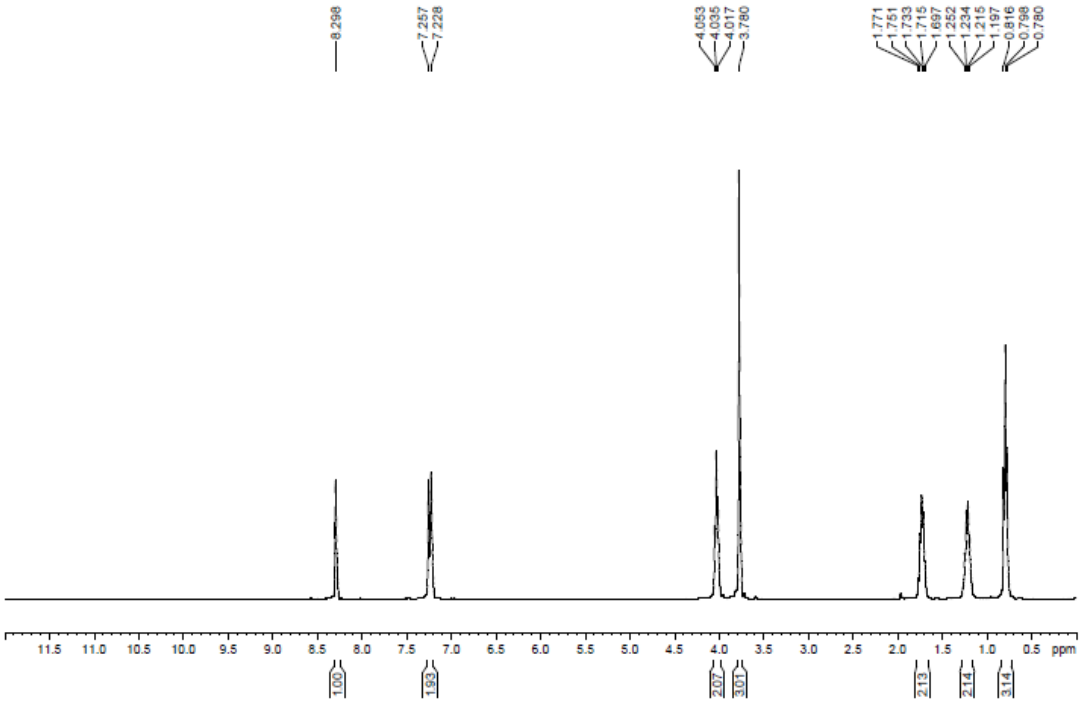


Fig.11. ***^{1}H NMR of BMIMPF$_6$***

The ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate was prepared as above the procedure. The various possibilities of impurities in imidazolium ionic liquids have been noted. In order to minimize possible halide and other impurities, UV-Vis spectra is taken. Fig. 12 indicates the UV-Vis spectra of 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid. The absence of any absorption peak below 290 nm indicated the absence of any colored impurities.

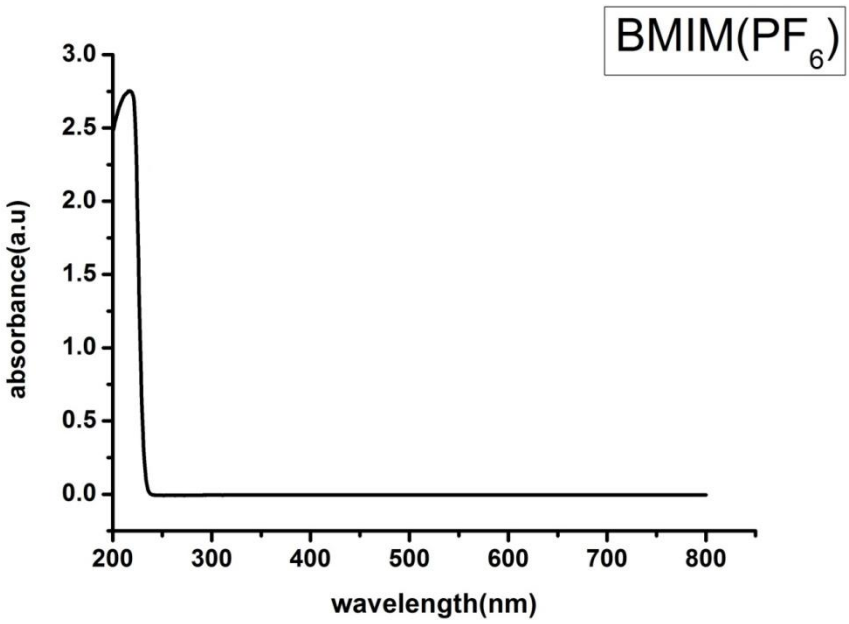


Fig.12. UV spectra of $BMIMPF_6$

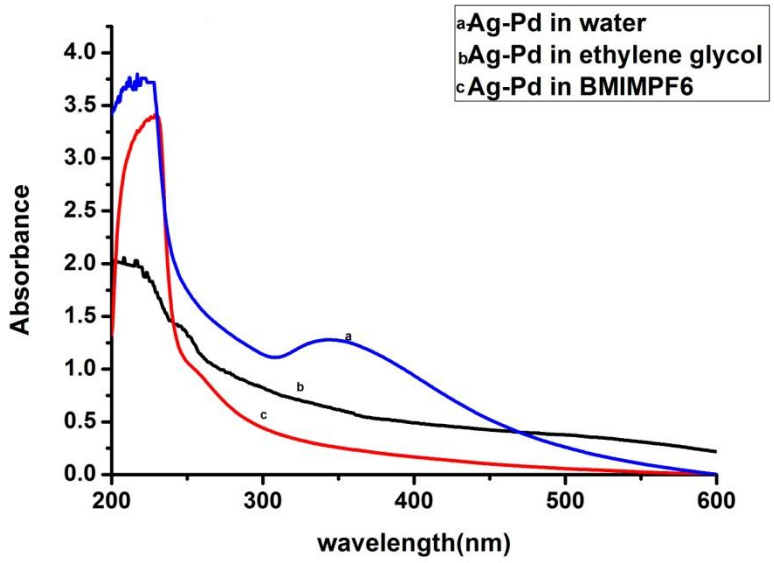
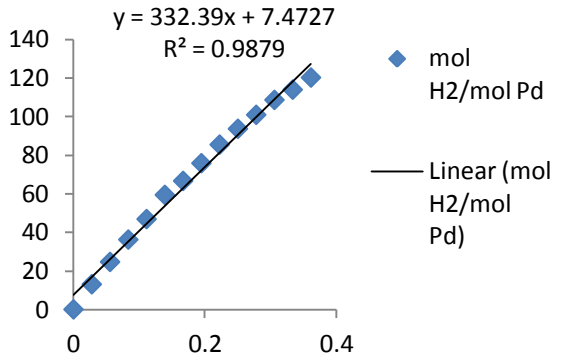


Fig.13. UV peak of (a) Agpd in water (b)Agpd in ethylene glycol (c)Agpd in $BMIMPF_6$ IL

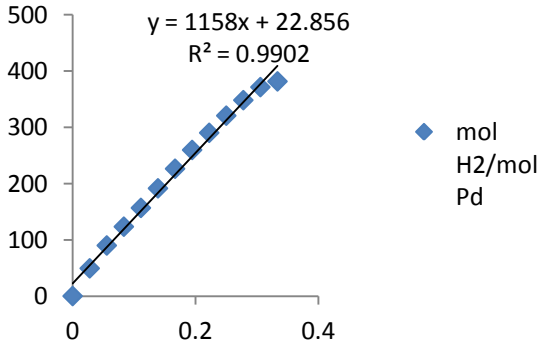
Absence of peak at 403nm confirms the formation of bimetallic nanomaterial. In case of water there is a peak, which was absent when ethylene glycol and $BMIMPF_6$ was taken as solvent this may be due to the viscosity of the solvent. $BMIMPF_6$ is more viscous than that of water and ethylene glycol which would affect the particle size.

3.2 Catalytic Activity of Metal Nanoparticle

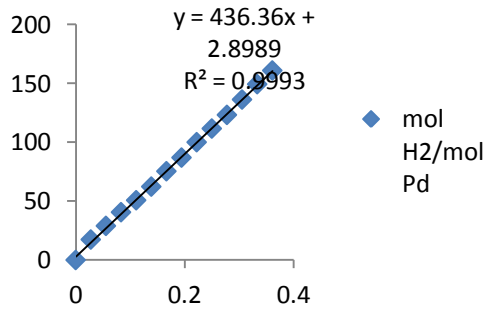
The catalytic activity of Pd and AgPd nanoparticles in different solvents was studied using differential pressure manometer. The catalytic activity was measured by calculating TON and TOF by employing a simple allyl alcohol hydrogenation reaction. Turnover numbers (TONs) for these catalysts were measured by H_2 consumption via differential pressure measurements. Turnover frequencies (TOFs) were calculated from the slope of TON vs. time graph which is shown below. Table 2 shows the TOF of Pd and AgPd bimetallic nanoparticle in different solvents.



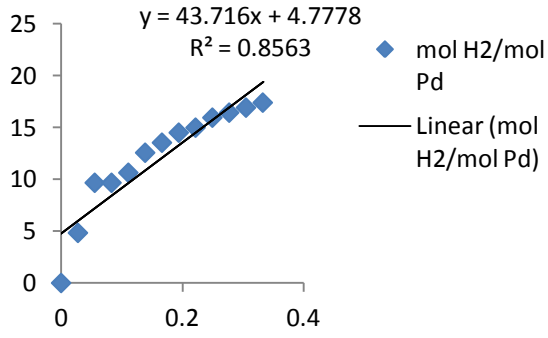
(a)



(b)



(c)



(d)

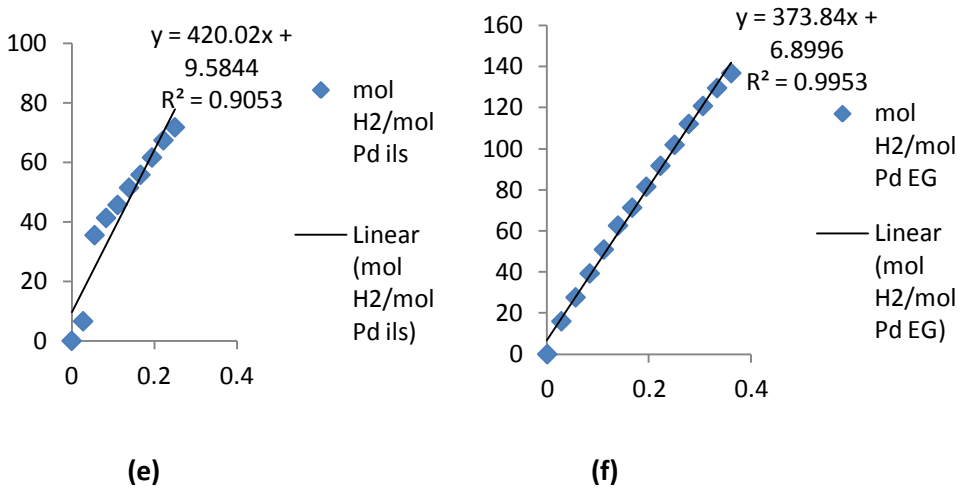


Fig.14 . Turn over frequency of hydrogenation of allyl alcohol in different media (a) AgPd nanoparticle in water (b) Pd nanoparticle in water (c) Pd nanoparticle in $BMIMPF_6$ (d) AgPd nanoparticle in $BMIM(PF_6)$ (e) Pd nanoparticle in ionic liquid $BMIMPF_6$ recycle (f)Pd nanoparticle in ethylene glycol.

In all the graph linear plot shows the TOF we got have minimum error.Y value gives the turn over frequency. Higher the value of R^2 shows the authentic and accuracy of the catalysis.

Table 2. **Catalytic activity of nanoparticle in different medium.**

Catalyst	**Solvent**	**Turn Over Frequency(TOF)**
Palladium nanoparticle	Water	1152
Silver-palladium nanoparticle	Water	332
Palladium nanoparticle	Ethylene glycol	373
Silver-palladium nanoparticle	Ethylene glycol	40
Silver-palladium nanoparticle	Ionic liquid ($BMIMPF_6$)	43
Palladium nanoparticle	Ionic liquid ($BMIMPF_6$)	436
Palladium nanoparticle recycle	Ionic liquid ($BMIMPF_6$)	420

The catalytic activity of the nanoparticle in the hydrogenation of allyl alcohol was mesured by differential pressure measurement. The monometallic and bimetallic nanoparticles were kept similar only differing the solvent i.e. water , ethylene glycol , ionic liquid ($BMIMPF_6$).

The above result shows that PVP-stabilized bimetallic nanoparticle in $BMIMPF_6$ can be used for wide range of hydrogenation reaction but ethylene glycol doesn't show any good result. Bimetallic nanoparticle in water shows the best activity having TOF 332. It can be clearly seen from the table-2 that the activities of the catalyst in IL-phase are not higher than water. However, the negligible-volatility and high thermal stability of $BMIMPF_6$ ILs may allow catalytic reaction in conditions not accessible by conventional solvents. Nanoparticle in ILs can be reused by removing all volatile product and substrate. From the above study it was clear that monometallic and bimetallic nanoparticle can be prepared in ethylene glycol without any reducing agent. When palladium nanoparticle was freshly used for catalytic hydrogenation of allyl alcohol it gives TOF equal to 436 , then the allyl alcohol and the products was removed and the left catalyst was again reused which gives TOF 420. From these data it was confirmed that nanoparticle can be reused.

4.Conclusion

Monometallic Pd and bimetallic Ag-Pd nanoparticle were synthesized in different solvent media and catalytic activities were studied. From the comparative study of catalytic activity of monometallic and bimetallic nanoparticle in different medium it was clear that nanoparticle shows high catalytic activity in water with higher value of TOF. Unreacted substrates and products were easily removed from the IL-phase under reduced pressure and the catalyst can be reused with change in catalytic activity. Further more studies are going on the comparative study of bimetallic nanoparticle in ionic liquid.

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